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<b>(21) International Application Number:</b> PCT/DK97/00344 <b>(22) International Filing Date:</b> 26 August 1997 (26.08.97) <b>(30) Priority Data:</b> 0910/96 29 August 1996 (29.08.96) DK <b>(71) Applicant (for all designated States except US):</b> DANFOSS A/S [DK/DK]; DK-6430 Nordborg (DK). <b>(72) Inventors; and</b> <b>(75) Inventors/Applicants (for US only):</b> BJERRUM, Niels, Jan-niksen [DK/DK]; Rådhusvej 59, DK-2920 Charlottenlund (DK). CHRISTENSEN, Erik [DK/DK]; Hellerupvej 1, DK-2900 Hellerup (DK). STEENBERG, Thomas [DK/DK]; Kildebakkegårds Allé 143, DK-2860 Søborg (DK). <b>(74) Common Representative:</b> DANFOSS A/S; Patent Dept., DK-6430 Nordborg (DK).	<b>(81) Designated States:</b> AM, AT, AU, BA, BG, BR, BY, CA, CH, CN, CZ, DE, DK, EE, ES, FI, GB, GE, HU, IL, IS, JP, KR, KZ, LT, LU, LV, MD, MK, MX, NO, NZ, PL, PT, RO, RU, SE, SG, SI, SK, TR, UA, US, UZ, VN, YU, Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TI, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).  <b>Published</b> <i>With international search report.</i>	
<b>(54) Title:</b> METHOD FOR ELECTROCHEMICAL PHOSPHATING OF METAL SURFACES, PARTICULARLY STAINLESS STEEL, AND APPLICATION OF AN AQUEOUS PHOSPHATING SOLUTION FOR SUCH A METHOD  <b>(57) Abstract</b> <p>A method for electrochemical phosphating of metal surfaces, particularly stainless steel, in connection with cold forming of metal workpieces, which method provides the cold formed work-piece with a lubricant after phosphating, involves an electrochemical phosphating through a cathodic process applying an aqueous phosphating solution containing: 0.5 to 100 g Ca<sup>2+</sup>/l, 0.5 to 100 g Zn<sup>2+</sup>/l, 5 to 100 g PO<sub>4</sub><sup>3-</sup>/l, 0 to 100 g NO<sub>3</sub><sup>-</sup>/l, 0 to 100 g ClO<sub>3</sub><sup>-</sup>/l and 0 to 50 g F<sup>-</sup> or Cl<sup>-</sup>/l, by which the temperature of the solution is between 0 and 95 °C, the pH-value of the solution is between 0.5 and 5, and the current density is between 0.1 and 250 mA/cm<sup>2</sup>. This gives a good lubrication effect, a good adhesion to the metal surface, particularly stainless steel, and a more expedient texture than ordinary phosphating.</p>		

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Method for electrochemical phosphating of metal surfaces, particularly stainless steel, and application of an aqueous phosphating solution for such a method

The invention concerns a method for electrochemical phosphating of metal surfaces, particularly stainless steel, in connection with cold forming of metal workpieces, which method provides the cold formed workpiece with a lubricant after the phosphating, particularly molybdenum disulphide or sodium stearate. The invention also concerns the application of an aqueous phosphating solution with a method of the kind described above.

In connection with cold forming of metal workpieces, e.g. steel workpieces, it is known that a better result is obtained if the cold formed workpiece is provided with a lubricant. It could be a glass-based lubricant melting during the strong heat development, thus having a lubricating effect, c.f. e.g. EP 0 043 639 B1 describing electroforetic application of a glaseous lubricant, in this case on a titanium workpiece, or the lubricant could be e.g. molybdenum disulphide or sodium stearate. To obtain a better adhesion of the lubricant on cold formed workpieces, a precoat is often added first.

Cold formed iron and standard steel workpieces are often provided with a precoat of zinc phosphate or zinc calcium phosphate, applied chemically during a pure immersion process, c.f. US 4, 517,029. This process is not used with stainless steel due to the increased corrosion resistance. Zinc phosphate can be applied on iron, standard steel and zinc-plated steel through an electrochemical process, c.f. e.g. EP 0 653 502 A2, however, this process is used for corrosion protection and provision of a substrate for paint.

Besides, it is known from Journal of Materials Science 29, 949-953 (1994) to provide stainless steel with calcium hydrogen phosphate through a similar process when producing bio-implants.

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Summing up, it can be stated that the state of the art shows an extensive use of lubrication of cold formed workpieces through immersion or dipping, whereas, to the best of our knowledge, electrochemical application has until now never been used for cold forming.

According to the invention, it has turned out that electrochemical phosphating of metal surfaces, particularly stainless steel, when cold forming metal workpieces, can be made with a good result, when a lubricant, as e.g. molybdenum disulphide or sodium stearate, is applied on the cold formed workpiece after the phosphating, when carrying through an electrochemical phosphating through a cathodic process using an aqueous phosphating solution containing:

0.5 to 100 g  $\text{Ca}^{2+}$ /l  
0.5 to 100 g  $\text{Zn}^{2+}$ /l  
5 to 100 g  $\text{PO}_4^{3-}$ /l  
0 to 100 g  $\text{NO}_3^-$ /l  
0 to 100 g  $\text{ClO}_4^-$ /l and  
0 to 50 g  $\text{F}^-$  or  $\text{Cl}^-$ /l

by which the temperature of the solution is between 0 and 95°C, the pH-value of the solution is between 0.5 and 5, and the current density is between 0.1 and 250 mA/cm<sup>2</sup>.

The addition of calcium to the phosphating solution involves some surprising improvements during precipitation, as calcium partly improves the initiation of the precipitation, partly provides a more dense layer than pure zinc phosphate. The improved initiation means that a lower current is required for the precipitation, and the increased density and thus the decreasing electrical conductivity of the precoat means that the process is less sensitive to the geometrical configuration of the workpiece to be phosphatised. Thus the coating of e.g. the inside of a cup

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is possible, without requiring a change of the geometrical configuration of the anode, which increases the applicability of the process substantially when compared with the known processes. Further, the addition of calcium gives a reduced friction when compared with pure zinc phosphate.

According to the invention methods in any of the claims 2 to 4 are expedient.

Thus, the invention concerns a method as stated in the describing part of claim 1, and this method is particular by using a solution as stated in the characterising part.

The invention also concerns the application of an aqueous phosphating solution as stated in any of the claims 1 to 4 for electrochemical phosphating of metal surfaces, particularly stainless steel, by which the cold formed workpiece are provided with a lubricant after the phosphating, particularly molybdenum disulphide or sodium stearate, particularly an application as stated in claim 6.

The present invention enables precipitation of a phosphate layer having a thickness appropriate for cold forming, and additionally the applied addition of calcium causes an improvement of the precipitation initiation, improves the applicability of the process for workpieces having a complicated geometrical configuration, and reduces friction. Additionally, a polymer, when added, is incorporated in and thus improving the coating. Besides, the addition of  $F^-$  gives a better adhesion, particularly to stainless steel surfaces, and thus a more expedient texture is obtained than with ordinary phosphating.  $Cl^-$  can be used instead of  $F^-$ . The application of  $NO_3^-$  and/or  $ClO_3^-$  limits the formation of bubbles on the workpiece surface.

The following table shows a number of examples demonstrating a series of typical test results obtained by using the method

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according to the invention. The properties of the precipitated coatings are tested through cup pressing, by which a piston is pressed against the workpiece placed in a die or a holder. When measuring the piston pressure as a function of the cup height, the decomposition of the lubricant film can be registered as an increase in the piston pressure caused by increased friction. The maximum cup height is the one at which the piston pressure has increased to the same level as the static piston pressure when starting the cup pressing.

It appears from the table that a known procedure (c.f. examples 1 and 1a) at a temperature of 70°C, pulsating current and a pulse-pause relation of 0.25 and a duration of the coating process of 10 minutes will give a maximum cup height of 27 mm; the obtained layer is very porous, has a poor adhesion and often is "caked", i.e. in the form of flakes. The application of an aqueous phosphating solution with the method according to the invention, c.f. examples 4 to 6, enables applying the precoat at temperatures as low as 25°C, without requiring special equipment for pulsation of the current, i.e. pure DC, and for a much shorter time, approx. 3 minutes. Additionally, larger cup heights can be obtained, c.f. examples 5 and 6. The use of a water soluble polymer, c.f. example 6, for which an ordinary, commercially available polymer (polyethylene glycol in the form of PEG 1000) is used, will give a more robust coating.

The coating obtained in accordance with the invention is very tight and uniform, facilitates the handling of cold formed workpieces, and permits transport without risking that the coating falls off. The method according to the invention can also be used in connection with other processes than cold forming, e.g. for corrosion protection and provision of a substrate for paint.

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## Examples

	Example No. 1 (comp.)	Example No. 1a (comp.)	Example No. 2 (comp.)	Example No. 3
[F <sup>-</sup> ]	0.02 M	0.02 M	0.02 M	0.02 M
[Zn <sup>2+</sup> ]	0.31 M	0.31 M	0	0.11 M
[Ca <sup>2+</sup> ]	0	0	0.44 M	0.22 M
[NO <sub>3</sub> <sup>-</sup> ]	0.62 M	0.62 M	1.09 M	0.65 M
[PO <sub>4</sub> <sup>3-</sup> ]	0.28 M	0.28 M	0.41 M	0.23 M
[ClO <sub>3</sub> <sup>-</sup> ]	0.20 M	0.20 M	0.32 M	0.24 M
pH	2	2	2	2
[Polymer]	0	0	0	0
Current density	45 mA/cm <sup>2</sup>	45 mA/cm <sup>2</sup>	45 mA/cm <sup>2</sup>	72 mA/cm <sup>2</sup>
Pulsation	0.5 s pulse 2 s pause	0.5 s pulse 2 s pause	none	0.5 s pulse 2 s pause
Time	10 min.	10 min.	5 min.	10 min.
Temperature	70°C	70°C	25°C	70°C
Workpiece material	stainless steel	stainless steel	stainless steel	stainless steel
Obtained layer thickness	43 ± 9 g/m <sup>2</sup>	43 ± 9 g/m <sup>2</sup>	65 ± 7 g/m <sup>2</sup>	47 ± 4 g/m <sup>2</sup>
Coating	Zn <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>	Zn <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>	Ca <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>	Ca <sub>0.5</sub> Zn <sub>2.5</sub> (PO <sub>4</sub> ) <sub>2</sub>
Lubricant	MoS <sub>2</sub>	Na-stearate	MoS <sub>2</sub>	MoS <sub>2</sub>
Lubricant layer thickness	12 ± 2	27 ± 5	21 ± 5	20 ± 8
Max. cup height (in mm)	16.7 ± 2.7	27.0 ± 1	24.4 ± 2.3	20.2 ± 1.6

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	Example No. 4	Example No. 4a	Example No. 5	Example No. 6
[F <sup>-</sup> ]	0.02 M	0.02 M	0.02 M	0
[Zn <sup>2+</sup> ]	0.06 M	0.06 M	0.06 M	0.06 M
[Ca <sup>2+</sup> ]	0.43 M	0.43 M	0.43 M	0.43 M
[NO <sub>3</sub> <sup>-</sup> ]	0.57 M	0.57 M	0.57 M	0.61 M
[PO <sub>4</sub> <sup>3-</sup> ]	0.89 M	0.89 M	0.89 M	0.33 M
[ClO <sub>3</sub> <sup>-</sup> ]	0	0	0	0
pH	2	2	2	2
[Polymer]	0	0	0	20 g PEG 1000/1
Current density	43 mA/cm <sup>2</sup>	72 mA/cm <sup>2</sup>	72 mA/cm <sup>2</sup>	30 mA/cm <sup>2</sup>
Pulsation	none	none	none	none
Time	3 min.	3 min.	3 min.	3 min.
Temperature	25°C	25°C	25°C	25°C
Workpiece material	stainless steel	stainless steel	stainless steel	stainless steel
Obtained layer thickness	26 ± 7 g/m <sup>2</sup>	44 ± 4 g/m <sup>2</sup>	44 ± 4 g/m <sup>2</sup>	42 ± 4 g/m <sup>2</sup>
Coating	Ca <sub>2</sub> Zn(PO <sub>4</sub> ) <sub>2</sub>	Ca <sub>2</sub> Zn(PO <sub>4</sub> ) <sub>2</sub>	Ca <sub>2</sub> Zn(PO <sub>4</sub> ) <sub>2</sub>	Ca <sub>1.6</sub> Zn <sub>1.4</sub> (PO <sub>4</sub> ) <sub>2</sub>
Lubricant	MoS <sub>2</sub>	MoS <sub>2</sub>	Na-stearate	Na-stearate
Lubricant layer thickness	28 ± 5	36 ± 7	18 ± 4	21 ± 6
Max. cup height (in mm)	22.7 ± 1.3	26.9 ± 1.1	>31.0	>31.0



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Patent Claims

1. Method for electrochemical phosphating of metal surfaces, particularly stainless steel, used with cold forming of metal workpieces, which method provides the workpiece with a lubricant after the phosphating, particularly molybdenum disulphide or sodium stearate, characterised in that an electrochemical phosphating is effected through a cathodic process using an aqueous phosphating solution containing
  - 0.5 to 100 g  $\text{Ca}^{2+}$ /l
  - 0.5 to 100 g  $\text{Zn}^{2+}$ /l
  - 5 to 100 g  $\text{PO}_4^{3-}$ /l
  - 0 to 100 g  $\text{NO}_3^-$ /l
  - 0 to 100 g  $\text{ClO}_3^-$ /l and
  - 0 to 50 g  $\text{F}^-$  or  $\text{Cl}^-$ /lby which the temperature of the solution is between 0 and 95°C, the pH-value of the solution is between 0.5 and 5, and the current density is between 0.1 and 250 mA/cm<sup>2</sup>.
2. Method according to claim 1, characterised in that the temperature of the solution is approx. 25°C, the pH-value is 1 to 4, and the current density is 5 to 250 mA/cm<sup>2</sup>.
3. Method according to claim 1 or 2, characterised in that the aqueous phosphating solution contains
  - 10 to 20 g  $\text{Ca}^{2+}$ /l
  - 2 to 10 g  $\text{Zn}^{2+}$ /l
  - 30 to 90 g  $\text{PO}_4^{3-}$ /l
  - 20 to 50 g  $\text{NO}_3^-$ /l
  - 0 to 40 g  $\text{ClO}_3^-$ /l and
  - 0 to 5 g  $\text{F}^-$ /l
4. Method according to any of the claims 1 to 3, characterised in that additionally the aqueous phosphating solution con-

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tains 0 to 100 g water soluble polymer per litre, particularly polyvinyl alcohol, polyethylene glycol and/or polyethylene oxide.

5. Application of an aqueous phosphating solution as stated in any of the claims 1 to 4 for electrochemical phosphating of metal surfaces, particularly stainless steel, in connection with cold forming of metal workpieces, which method provides the workpiece to be cold formed with a lubricant after phosphating, particularly molybdenum disulphide or sodium stearate.
6. Application according to claim 5, characterised in that additionally the phosphating solution contains 0 to 100 g water soluble polymer per litre, particularly polyvinyl alcohol, polyethylene glycol and/or polyethylene oxide.

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## INTERNATIONAL SEARCH REPORT

International application No.  
PCT/DK 97/00344

## A. CLASSIFICATION OF SUBJECT MATTER

IPC6: C25D 11/36

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC6: C25D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE,DK,FI,NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

WPI, EDOC, JAPIO

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	EP 0653502 A2 (TOYOTA JIDOSHA KABUSHIKI KAISHA), 17 May 1995 (17.05.95), page 4, line 32 - page 6, line 22; page 7, line 5 - line 35, claims 8-12,15, 17	1-6
Y	WO 9119836 A1 (HENKEL CORPORATION), 26 December 1991 (26.12.91), page 3, line 23 - page 6, line 16; page 6, line 35 - page 7, line 6; page 7, line 21 - line 31, claims 1,4,5, abstract	1,2,4-6
Y	US 4874480 A (SAKAE SONODA ET AL), 17 October 1989 (17.10.89), column 1, line 1 - line 21; column 2, line 18 - line 62; column 3, line 47 - line 49, column 5, line 5 - line 11, claims 1-12, abstract	1,2,4-6

☒ Further documents are listed in the continuation of Box C.☒ See patent family annex.

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Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	Patent Abstracts of Japan, Vol 11, No 242, C-438 abstract of JP 62-50496 A (NIPPON KOKAN K.K.), 5 March 1987 (05.03.87)	1-6

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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0653502 A2	17/05/95	JP 7138766 A JP 7138764 A JP 8013154 A	30/05/95 30/05/95 16/01/96
WO 9119836 A1	26/12/91	JP 4036498 A	06/02/92
US 4874480 A	17/10/89	DE 3812692 A EP 0288853 A,B SE 0288853 T3 JP 63262500 A	24/11/88 02/11/88  28/10/88

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